A First Principle Study of Layered Transition Metal Dichalcogenides and Reconstructed Germanium Surfaces

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Introduction

The study of layered materials is the field related with low dimensional physical systems that are the subject of much great interest currently [1–67]. In particular, the study of layer dependent electronic and dielectric properties of these materials is not only interesting from a basic point of view but has also a strong technological potential. Furthermore, electronic transport in these materials is a topic of interest for both technological applications and fundamental understanding of basic physical phenomena. The continuous demand for smaller and faster devices has pushed the conventional device geometry from bulk towards lower dimensions such as 2D electron gases (2DEGs) in heterostructure quantum wells [68] and graphene [69–71], and 1D electron gases (1DEGs) in nanowires [72] and carbon nanotubes(CNTs) [73]. The reason for this shift of bulk geometry towards lower dimensions is to enhance the carrier mobility in a single transistor and to have large number of transistors on a single chip for faster switching operation and lower power consumption. With the continuous advances in semiconductor technology, the dimensions of heterostructures and devices fabrication have already entered in the regime of quantum mechanics. Consequently, the study of nanostructures has become an active area of research in the field of emerging nanoscience.

On the other hand, surfaces are another typical example of low dimensional physical systems. Nowadays, the great interest in taking advantage of the properties discovered and predicted by the emerging nanoscience makes the surface and interface science a key research area [74–77]. The main reason for this is that typically a surface is nothing else than the template on which some nanomaterials are constructed. Therefore, surfaces are the laboratories where research at the nanoscale can be done. Thus, fundamental understanding of the atomic-scale processes taking place at surfaces as well as their intrinsic properties, are also key factors for nanoscience and nanotechnology. The demand of novel materials and fundamental understanding of their properties, is the driving force behind material science in the 21^{st} century. The researcher's aim is to design new materials which suit particular industrial applications.

One of the economical and easiest way of predicting new materials is by first principles calculations. The idea behind first principle, also known as ab-initio, calculation is to apply the basic laws of physics to identify the stability of the materials in different compositions as well as their fundamental properties. Materials are made of atoms which are the building blocks of matter/materials. The atoms themselves consist of electrons. The behavior of a material predicted by carrying out electronic structure calculations is a well known fact today and has many successes behind it [78–80]. However, the success [81] of first principles calculations in predicting new materials and offering in-depth explanation of observations made in the experiments can be attributed to intensive and extensive research in the field of condensed matter. Various theories have been developed, starting from Hartree to the most popular framework of modern density functional theory. The other reason for the success of ab-initio based physics is the rapid development of computer technology. With the increasing power of computers, ab initio methods are becoming an essential tool in physics, chemistry, biology and materials science [82]. However, it is also important to mention that predictions made by ab-initio calculations are more useful when backed up by experimental synthesis of the predicted material.

Review of Literature

Layered materials such as transition metal dichalcogenides, MX_2(M=Mo, W, Nb; X=S, Se, Te), represent a diverse and large untapped source of low dimensional systems with exotic electronic properties and high specific surface areas, that are important for sensing, catalysis and energy storage applications [83–101]. In all the layered materials intralayer bonding is very strong

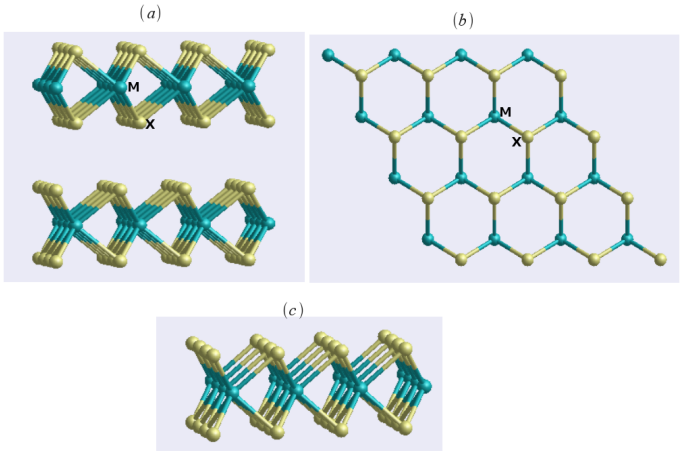

Figure 1: (a) Side view of the crystal structure of bulk LTMDs(van der Walls bonded MX_2(M=Mo,W,Nb; X=S,Se,Te) units) (b) Top view of both bulk and monolayer LTMDs (c) Side view of monolayers of MX_2.

compared to interlayer bonding which is weak. The bulk crystal of, Layered transition metal dichalcogenides(LTMDs) on which we mainly focus in our work, is built up of van der Walls bonded chalcogen(X)-metal(M)-chalcogen(X) units which crystallizes in hexagonal structure(2H symmetry having space group $P6_3/mmc$) [83] consisting of X-M-X layers as shown in figure 1. 2H-MX_2 i.e. bulk structure has two such layers, each of the stable units referred as a monolayer(1H-MX_2) which consists of two hexagonal planes of chalcogen atoms and an intermediate sandwiched hexagonal plane of metal atoms. Because of the weak interactions between the layers and the strong interactions within the layers, the formation of ultrathin crystals of $1H - MoS_2$ by the same micromechanical cleavage technique, as was applied to graphene, has been achieved by Novoselov et. al. [102]. They extracted $6.5\mathring{A}$ thick monolayer with honeycomb structure.

Due to the weak forces between the layers and the anisotropic character of LTMDs, shearing takes place more easily, leading to these being put into lubricant applications [84]. LTMDs find application in photocatalysis, optoelectronics and photovoltaics as well [83, 87–89, 92, 94]. LTMDs have been found to show many interesting optical properties including excitonic effects in these materials [83, 103–106] which are important for device applications. An extensive survey of the properties of bulk LTMDs have been made by Wilson and Yoffe [83, 86]. Beal et. al. [103] measured the transmission spectra in the energy range of 0-4.0 eV and, Beal and Hughes [104] measured the reflectivity spectrum for $\overrightarrow{E} \perp c$. Hughes and Liang [105] measured the vacuum ultraviolet reflectiv-

ity spectra in the range of 4.5-14 eV for $\overrightarrow{E} \perp c$. Zeppenfeld [107] measured the electronic energy losses and optical anisotropy of single MoS_2 crystal. Liang and Cundy [108] has made detailed study of the electron energy loss spectra of LTMDs. Previous research found that bulk MX_2(M=Mo, W; X=S, Se, Te) have a band gap of 0.7 eV to 2.0 eV [63,85,87,90,91,96–99,101] which can make these materials as a candidate for device applications and may be promising replacement of Silicon(Si).

Furthermore, Group-IV semiconductor materials, including Si and Ge, play an important role in modern technology. Metal/semiconductor interface interactions continue to attract interest in both fundamental and applied research [74–77, 109–113] and are of vital importance for the semiconductor and microelectronic industry. With miniaturization pushing into the nanoscale regime, new ways of constructing nanoscale devices are being looked into. Physical properties of semiconductor surfaces play an important role in the miniaturization of devices. Generally the focus lies on metal/Si interface because of the

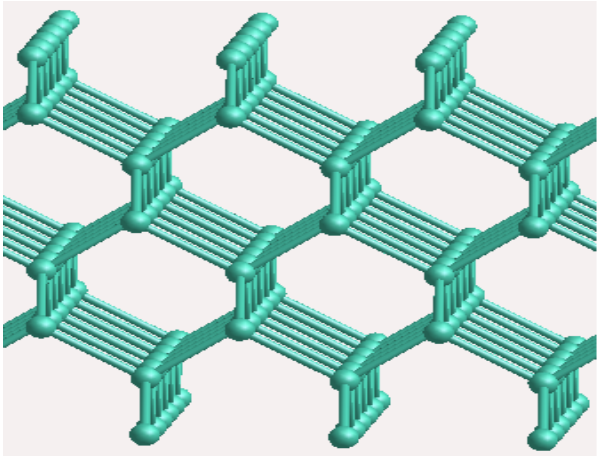

Figure 2: Side view of unreconstructed clean(001) surface of group-IV element(Si and Ge). Surface atoms are bonded with two atoms of subsequent layer, therefore, there are two dangling bonds on each surface atom.

importance of Si in semiconductor industry. The metal/Ge interface is less well studied, despite its importance in the development of radiation detector systems and high speed electronic devices. Presence of broken (dangling) bonds on these surfaces determine their physical and chemical properties [114–116]. These surfaces have two dangling bonds on the each surface atom(Figure 2). These surfaces minimize their energy by adjusting the positions of their atoms (i.e. undergo reconstruction) leading to reduction in the number of the dangling bonds. Dangling-bond surface states are particularly interesting because they are closely related to the position of the Fermi level [117] and possibly related to the surface reconstruction effects [78]. Among the most stable surfaces of Si and Ge, that so far have received attention from technological perspective, are the reconstruction of Si(001) and Ge(001) surfaces [114–132], in particular, those having lower indexes, namely: (2x1), (2x2) and (4x2). In the reconstruction, dimer formation on the top of a slightly relaxed substrate on the surfaces is the result of partial dangling bond saturation. Further stabilization of the surface

is reached by a distinct buckling of the dimers. Furthermore, adsorption of noble metal atoms on these surfaces to create exotic low dimensional structures such as nanowires has been of leading interest currently [74–77,112,113]. Gurlu et. al. [109] were the first to observe experimentally the nanowire formation on Ge(001) surface after deposition of roughly 0.25 monolayer of Pt. They observed one-atom thick wires which could be hundreds of nanometers long. It has also been observed that there could appear different types of reconstruction depending upon the noble metal coverage and annealing temperature [133–135].

Theoretical Background

The properties of condensed matter and molecules are determined by the electrons and the nuclei. The study of electrons provides salient information about electronic, magnetic, optical and bulk properties of matter [81, 82]. Various electronic structure methods have been developed in the past [79, 80]. The most prominent ones used for solid systems are Density Functional Theory (DFT) [136,137]. The main goal of any density-functional based computational method is to calculate properties, for given chemical composition and geometrical structure of a system, as accurately as possible by solving the electronic Schrodinger equations [138]. This method does not make use of any empirical information or free parameters. However, the problem of solving Schrodinger equations to find quantum ground state description of the electrons in a condensed system is a correlated many-body problem, which at present can be solved only approximately and yet provides fairly accurate values.

A complete description of the quantum mechanical behavior of atoms requires detailed consideration of interactions between electrons and nuclei. The starting point of the description of a system containing electrons and nuclei is the Hamiltonian:

$$H = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \frac{\hbar^2}{2M_I}\sum_I \nabla_I^2 - \sum_{i,I}\frac{Z_I e^2}{|r_i - R_i|} + \frac{1}{2}\sum{}' \frac{e^2}{|r_i - r_j|} + \frac{1}{2}\sum{}' \frac{Z_I Z_J e^2}{|R_I - R_J|} \tag{1}$$

where m_e and M_I represent the electron mass and mass of the nuclei respectively, r_i and R_I are positions of electron and nuclei. Z_I is charge of nuclei and e is charge of electron. The first and second terms are the kinetic energies of the electrons and nuclei, respectively. The third term describes the Coulomb attraction between nuclei and electrons. The fourth and fifth terms describe the electron-electron and nucleus-nucleus Coulomb repulsion, respectively. Since the real Hamiltonian of solids consists of electrons and nuclei of the order of 10^{23} the problem is impossible to solve. So we need new approximations to solve the many-body problem.

Born-Oppenheimer approximation

Born-Oppenheimer approximation is the early approximation used to solve the Hamiltonian by considering the fact that the nuclei can not move as much as electron due to its heavy mass. Based on that observation, it has been assumed that as a first approximation the motions of the two subsystems (electrons and

nuclei) can be uncoupled i.e. the electrons move in the field of fixed nuclei. Thus, within this approximation, the kinetic energy of nuclei can be neglected and the coulomb repulsion interaction between the nuclei is considered as a constant. The remaining terms in the Hamiltonian describe the motion of electrons in the field of fixed nuclei charges, which is commonly called electronic Hamiltonian [81]. If we have N electrons moving in the external potential(V_{ext}) of fixed nuclei, then the electronic Hamiltonian in atomic units $\hbar = m = |e| = 1$ can be written as:

$$H = -\frac{1}{2}\sum_i \bigtriangledown_i^2 + \sum_i V_{ext}(r_i) + \frac{1}{2}\sum_{ij}{}' \frac{1}{r_{ij}} \tag{2}$$

Even after omitting the nuclei terms in old Hamiltonian still the electrons are in the order of 10^{23} making an exact solution impossible. To get rid of the still unsurmountable problem of all electron equation, variational method is often used [81, 139]. It is a powerful method which allows one to choose any approximate wave-function and looking for lower energy by making $\langle H \rangle$ stationary. It offers a way of searching for ground state wave-function. However, complicated nature of electron-electron interactions makes it difficult to solve many-electron Hamiltonian, this is where we are forced to make approximation for the wave-function.

Hartree and Hartree-Fock Approximations

In Hartree approximation, each electron is moving independently in some sort of average potential of the rest of electrons. Therefore, the wave function can be approximated as

$$\psi_H = \prod_i \phi_i(r_i) = \phi_1(r_1)\phi_2(r_2)\phi_3(r_3)... \tag{3}$$

where product is carried over all the occupied orbitals ϕ_i. The least possible ground state orbitals are determined using variational principle by making $\langle H \rangle$ stationary. We can make ψ_H better by taking care of antisymmetric nature of the wave-function [81, 82, 139]. Electron also has spin, so the corresponding spin wave-function is also brought in Hartree-Fock Theory. The Hartree-Fock approximation is viewed as the basis or foundation for more accurate approximation involving correlation between electrons. Within the Hartree Fock approximation, the many body wave function of the system can be treated as a single Slater determinant of independent electrons which satisfies antisymmetry rule. The total wave function $\psi_{HF}(r_1, \sigma_1 ..... r_N, \sigma_N)$ can be then written as:

$$\psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1,\sigma_1) & \psi_1(x_2,\sigma_2) & \psi_1(x_3,\sigma_3) & .. & .. & \psi_1(x_N,\sigma_N) \\ \psi_2(x_1,\sigma_1) & \psi_2(x_2,\sigma_2) & \psi_2(x_3,\sigma_3) & .. & .. & \psi_2(x_N,\sigma_N) \\ \psi_3(x_1,\sigma_1) & \psi_3(x_2,\sigma_2) & \psi_3(x_3,\sigma_3) & .. & .. & \psi_3(x_N,\sigma_N) \\ \vdots & \vdots & \vdots & & & \vdots \\ \vdots & \vdots & \vdots & & & \vdots \\ \psi_N(x_1,\sigma_1) & \psi_N(x_2,\sigma_2) & \psi_N(x_3,\sigma_3) & .. & .. & \psi_N(x_N,\sigma_N) \end{vmatrix}$$

where the $\psi_1(x_1, \sigma_1)$ are single particle spin orbitals.

Hartree-Fock theory provides an exact treatment of exchange correlation useful for calculations of molecules and larger N-body systems. The expectation value of the Hamiltonian with the wave function is described as [81, 139]:

$$\langle\psi_{HF}|H|\psi_{HF}\rangle = -\frac{1}{2}\sum_{i,\sigma}\int \phi_i^{\sigma*}(r) \bigtriangledown^2 \phi_i^{\sigma}(r)dr + \sum_{i,\sigma}\int \phi_i^{\sigma*}(r)V_{ext}(r)\phi_i^{\sigma}(r)dr$$
$$+\frac{1}{2}\sum_{i,j\sigma_i,\sigma_j}\int \phi_i^{\sigma*}(r)\phi_j^{\sigma*}(r')\frac{1}{|r-r'|}\phi_i^{\sigma_i}(r)\phi_j^{\sigma_j}(r')drdr'$$
$$-\frac{1}{2}\sum_{i,j\sigma}\int \phi_i^{\sigma*}(r)\phi_j^{\sigma*}(r')\frac{1}{|r-r'|}\phi_i^{\sigma}(r)\phi_j^{\sigma}(r')drdr' \quad (4)$$

Where first term represents the kinetic energy, second term the external energy, the third term describes the direct interactions among electrons(or coulomb energy with self interaction), while the exchange interaction is described by the fourth term. Notice that exchange energy exists between the orbitals of same spin i.e. either $\sigma = 1/2$ or $-1/2$, otherwise it is zero. Exchange energy is purely quantum-mechanical contribution coming from the antisymmetric nature of the wave function. It can be interpreted in terms of exchange or Fermi hole which results from the deficit of electron(of same spin at $\overrightarrow{r'}$) in the neighborhood of $\overrightarrow{r}$. This leads to lowering of total energy because electrons are not interacting strongly as they would have otherwise.

If we want to go beyond the exchange interactions, then we have to take care of the interactions between the electrons of opposite spins which leads to the correlation energy. This makes wave functions more diffused and results into deeper hole and leads to further reduction in the total energy [139]. It can also be interpreted in terms of coulomb hole which results from the deficit of electron(of opposite spin at $\overrightarrow{r'}$) in the neighborhood of $\overrightarrow{r}$.

Foundation of Density Functional Theory

The ab initio method which will be used in the present research problem relies on Density Functional Theory (DFT). DFT, among the ab-initio methods, is now one of the most widely used approaches to the many-body electron problem [82,138]. It is in principle exact theory for interacting electrons, but in practice, it is an approximate methodology in terms of single electron equations. It is worth mentioning about the term '*functional*' which is the central part of entire DFT both mathematically as well as physically. Mathematically, functional is a map from a function to a number. In other words, functional takes a function as an input and gives a number as output or it takes range of numbers as an input via a function and gives a single number as an output. $F[f] = \int_{-1}^{1}(x^2+1)\mathrm{dx}$ is an typical example of functional [82]. Also area under curve $A[y] = \int_{x_1}^{x_2} y(x)dx$ provide a classical example of functional. Similarly, physically speaking, density functional can be defined as:

$$\rho[\psi] = \int_{-\infty}^{+\infty} \psi^*(r)\psi(r)dr \quad (5)$$

where density ρ is functional of wave function ψ and ψ further depends on the range of spatial coordinates r.

Hohenberg-Kohn Theorems

The DFT was developed by Hohenberg, Kohn and Sham which is based on the electronic density distribution $\rho(r)$ rather than the many electron wave function ψ [136,137]. In this framework the basic theorems of Hohenberg-Kohn(HK) have a fundamental importance.

The original theorem states that an exact representation of the ground state properties of a stationary, non relativistic many-particle systems in terms of the exact ground state density is possible. First HK theorem states that *the system of interacting particles in external potential $V_{ext}(r)$ is determined uniquely by ground state density, $\rho_0(r)$*. Therefore, two systems should be defined by their unique ground state electron density or there exists one-to-one correspondence between the ground state density of a system and the external potential [81, 139]. In other words, two external potentials differing by more than a constant lead to two different ground state densities. Since the Hamiltonian is uniquely determined by the external potential, it follows that all properties, including excited states, of the system can be regarded as functionals of the ground state density.

Second HK theorem states *that ground state energy can be written as a functional of density and the density $\rho(r)$ that minimizes the energy is the exact ground state density.* Thus the ground state energy as a functional of density can be written as:

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{ext}[\rho] = F[\rho] + \int V_{ext}(r)\rho(r)dr \tag{6}$$

The only inputs into the functional $E[\rho]$ that are unique to a given system are $V_{ext}(r)$, the electrostatic potential created by the nuclei and the total number of electrons N. $F[\rho] = T[\rho] + V_{ee}[\rho]$ is a universal functional which is independent of nuclear arrangement and charge. Unfortunately, it is this contribution which remains unknown, otherwise all electronic ground states for any nuclear configuration could be determined.

DFT lays the groundwork for approaches that are more accurate than Hartee-Fock through the inclusion of correlation energy, and less complicated due to its use of the three coordinate electron density as compared to 3N coordinate electron wave function [82]. The realization of accuracy depends upon how well $F[\rho]$ is approximated. An additional strength of DFT based methods is the fact that, since $F[\rho]$ is universal, better approximations to $F[\rho]$ have the potential of improving all DFT calculations, regardless of systemic details.

Kohn-Sham Formulation

Almost any practical use of DFT rely on the work of Kohn and Sham (KS) from the late 60's [136]. The Kohn-Sham equations result from an attempt to circumvent the problem of the unknown $F[\rho]$ by reformulating it as follows [137]:

$$F[\rho] = T_S[\rho] + V_H[\rho] + E_{XC}[\rho] \tag{7}$$

where $E_{XC}[\rho]$ is

$$E_{XC}[\rho] = T[\rho] - T_S[\rho] + V_{ee}[\rho] - V_H[\rho] \tag{8}$$

$T_S[\rho] = -\frac{1}{2}\sum_i^N \int \phi_i^*(r) \bigtriangledown^2 \phi_i(r) dr$ denotes the kinetic energy for a system of N non interacting electrons and $E_{XC}[\rho]$ is called exchange-correlation energy which contains the difference in kinetic energy between a system with N interacting electrons and one with N non interacting electrons. It also contains non classical part of $V_{ee}[\rho]$, both the exchange part captured in Hartee-Fock, and the correlation energy missed by Hartee-Fock.

Kohn-Sham theory is based on a basic ansatz, namely that the ground state density, $\rho(r)$, of an interacting system is also the ground state density of a non-interacting system with an effective potential $V_{eff}(r)$. The electron density is, therefore, determined from a single-particle Schrodinger equation:

$$[-\frac{1}{2} \bigtriangledown^2 + V_{eff}(r)]\phi_i(r) = \epsilon_i \phi_i(r) \tag{9}$$

where $\phi_i(r)$ are the single electron KS orbitals giving the density:

$$\rho(r) = \sum_i |\phi_i(r)|^2 \tag{10}$$

where the sum is over the occupied states. The effective potential $V_{eff}(r)$ is given by:

$$V_{eff}(r) = V_{ext}(r) + \frac{\delta}{\delta\rho(r)}[E_H + E_{XC}] \tag{11}$$

The Kohn-Sham energy functional that needs to be calculated is:

$$E[\rho] = T_S[\rho] + \int V_{ext}[\rho]\rho(r)dr + \frac{1}{2}\int\int \frac{\rho(r)\rho(r')}{r - r'} dr dr' + E_{xc}[\rho] \tag{12}$$

To solve the Kohn-Sham equation, we need to define V_{eff}, for defining it we must know electron density and to know electron density, we must know the single electron orbitals(or wave-functions). To break this circle, the problem is usually treated in a iterative way [81, 82, 139].

1. Define set of orbitals $\phi_i(r)$ to construct initial electron density

$$\rho(r) = \sum_i |\phi_i(r)|^2$$

2. Calculate the effective potential $V_{eff}[\rho]$.

3. Solve Kohn-Sham equation for the single particle wave function $\phi_i'(r)$.

4. Calculate the new electron density

$$\rho'(r) = \sum_i |\phi_i'(r)|^2$$

5. If the solution is self-consistent, then compute total energy. If solution is not self-consistent, then go to step 2 and calculate the $V_{eff}(r)$ by updating the electron density to get self consistent solution.

The iterations are continued until a desired convergence in electron density ρ and associated energy $E[\rho]$ are attained. Upon convergence, the ground state energy is found from the energy functional of Eq.(15). The validity of effective implementation of the Kohn-Sham method lies in finding a good approximation for E_{XC} and hence V_{eff}.

Local Density Approximation(LDA)

In principle, solution of Kohn-Sham equations with the exact exchange-correlation potential, would give a set of single particle eigenstates whose density of states equals that one of the fully interacting system. Unluckily the exact exchange-correlation potential is not known and one has to find reasonably approximations for V_{XC}. The simplest approach is the local density approximation(LDA) where the contribution of each volume element to the total exchange correlation energy is taken to be that of an element of a homogeneous electron gas with the density corresponding to that point [81,139,140]. In this approximation inhomogeneous systems are replaced with a constant density of homogeneous electron gas.

$$E_{XC}^{LDA}[\rho(r)] = \int \epsilon_{xc}^{homo.}[\rho(r')]\rho(r')dr' \tag{13}$$

where $\epsilon_{xc}^{homo.}$ is the exchange-correlation energy density of a homogeneous electron gas. E_{XC}^{LDA} is a good approximation for a slowly varying electron density and becomes exact for a uniform electron gas. Surprisingly, it sometimes performs well even with rapidly varying electron densities, however, with highly localized electron states it typically fails [82].

Generalized Gradient Approximation(GGA)

For a long time the local density approximation was considered the method of choice in electronic structure calculations. One strategy to improve the LDA is to include the gradient of the charge density in exchange-correlation functional, something that should take into account the inhomogeneity of the electron gas [81, 141]. The resulting method, where the exchange-correlation potential is a function of both the charge density at a given point, and the first-order gradient of the charge density at the same point, is known as the generalized gradient approximation (GGA).

$$E_{XC}^{GGA}[\rho(r)] = \int \epsilon_{xc}[\rho(r'), |\nabla\rho(r')|]\rho(r')dr' \tag{14}$$

Generally GGA is more accurate than LDA in comparison with experiments but computationally more time consuming than LDA.

It is important to mention that the KS eigenvalues, ϵ_i are not the true energy levels of the interacting system. The density $\rho(r)$ is one of the few physical quantities that can be strictly obtained, at least in principle, from KS formalism. In particular, the total energy is not equal to the sum of KS eigenvalues i.e. $E_{KS}[\rho(r)] \neq \sum_i^N \epsilon_i$ [139]. The KS Hamiltonian is an effective one-electron Hamiltonian that introduces the effects of electron-electron interactions in a mean-field approach. Although not exact, the KS eigenvalues (ϵ_{KS}) have proven

to be a reasonable starting point to understand the electronic structure of real systems. There are well known limitations in the KS band structure. In this context, it is important to mention that the fundamental band gap (E_g) of a semiconductor or insulator is only approximately predicted using the LDA or GGA exchange-correlation functionals. One of the reasons for that in the KS approach the gap, E_{KS}, is defined as the difference between the lowest unoccupied(ϵ_{KS}^{lumo}) and highest occupied (ϵ_{KS}^{homo}) eigenvalues which differs from the definition of the gap E_g [139]. The latter is defined as $E_g = I - A$, where I is the ionization potential and A the electron affinity. The relation between E_g and E_{KS} is given by $E_g = E_{KS} + \delta_{xc}$, where δ_{xc} is the derivative discontinuity, i.e., a finite kink that the exchange-correlation potential exhibits as the particle number crosses the integer number of particles N in the system.

Computation Method

The electron wave-function of Kohn-Sham orbitals can be expanded using a given basis set. These basis sets can be made from localized atomic orbitals, plane-wave or some mixed basis set. Depending upon different basis sets many simulation packages like VASP [142], WEIN2K [143], Elk [144], SIESTA [145], CASTEP [146] etc. have been developed to solve Kohn-Sham equations. In our case, all the calculations will be carried out using SIESTA method and the corresponding code(Spanish Initiative for Electronic Structure with Thousand of Atoms) [147–151] which uses localized basis sets of atomic orbitals [152–155]. This code is chosen due to its widespread use and efficiency. Moreover our motivation to use SIESTA is also there because it is freely available open source package and our computational resources along with computational time are compatible with it. One of the main characteristics of SIESTA is that it utilizes a very general and flexible linear combination of numerical atomic orbitals (LCAO) DFT method. While limited basis sets offer an advantage for large-scale simulation over traditional plane-wave techniques. The real promise lies in the development of new O(N) methods with a computational cost that scales linearly with system size. So it can be implemented for larger systems of thousands of atoms unlike other codes. Apart from that, the method is also characterized by a set of parameter that controls the accuracy of the self-consistent KS solution. For example the size (number of atomic basis orbitals) and range (radius of the basis orbitals) of the basis set, the fineness of real-space integration grid, the non-linear core correction to treat exchange-correlation interaction between core and valence states, etc.

Pseudopotential

The electrons in the atom can be divided in two groups, core and valance electrons. Core electrons reside in the deeper shells and are strongly bound to the nuclei. As a consequence, the core electrons are not strongly affected by the chemical environment in which the atom is embedded and they usually donot participate in the chemical bonding [156]. However, from the numerical point of view, these core electrons represent a very high computational cost. To reduce the numerical cost, in many DFT implementations, the external potential $V_{ext}(r)$ is replaced by the pseudopotential. In pseudopotential approximation,

the strong nuclear potential and core electrons are replaced by an effective ionic potential acting on the valance electrons [157, 158]. The pseudopotentials are typically generated for free atoms, but can be applied to solids and molecules since the core states almost remain the same. In SIESTA one typically uses norm-conserving pseudopotntial of the Troullier-Martins [159,160] type in which the norm of the pseudowavefunction is same as the one of the true wave function and beyond the cutoff radii pseudo-charge density as well as the pseudo valance orbitals are equal to the real ones.

Basis Sets

In the numerical solution to the KS equations one expands the wave functions in terms of a basis set:

$$\psi_n(r) = \sum_m c_{nm}\phi_m(r) \tag{15}$$

In SIESTA the basis orbitals are localized functions centered on the atoms [152–155]. At an atomic position R_I, the set of orbitals are

$$\phi_{I,lmn}(r) = \phi_{ln}(|r_I|)Y_{lm}(r_I) \tag{16}$$

where $r_I = (r) - R_I$, ϕ_{ln} is a radial function and Y_{lm} are the real spherical harmonics with angular momentum labeled by l,m. For each value of l one can have multiple radial functions labeled by n. A single-ζ(SZ) basis set have n = 1, double-ζ have n = 1, 2, etc. In the case of carbon, the minimal basis set (SZ), consists of a single s−orbital(l = 0, m = 0) and three p−orbitals (l = 1, m = 1, 0, 1), corresponding to the four valence electrons. This basis can be expanded by five polarization d−orbitals (l = 2, m = 2, −1, 0, +1, +2), and is denoted as single-zeta-polarized (SZP). If n = 2 the basis is denoted double-zeta-polarized (DZP) which is generally considered as the standard basis set in SIESTA. The radial functions have a finite range and are strictly zero beyond a cutoff radius.

Calculations with SIESTA

In order to solve the Kohn Sham differential equations one needs to specify the boundary conditions for the problem. In the SIESTA method one uses periodic boundary condition within the supercell approach [151]. This is the natural choice for bulk crystals, which in reality are periodic. The supercell approach can also be applied to non-periodic structures if a sufficient amount of vacuum is included in the supercell, to effectively separate the objects. In this way molecules, wires, and surfaces can be studied by including vacuum in three, two, or one directions, respectively.

Band Structure

Since the supercell is periodic, Bloch's theorem applies and the wave functions can be written as:

$$\psi_{nk}(r) = u_{nk}(r)e^{\iota k.r} \tag{17}$$

where $u_{nk}(r)$ has the periodicity of the supercell, k is a wave vector in the first Brillouin zone (BZ), and n is the band index. The above equation allows mapping the KS equations to the reciprocal space, where they are solved for each different k and the size of the problem is restricted to the number of orbitals in the supercell. The expectation value of a typical operator, $\hat{A}$, is found as:

$$\langle A \rangle = \frac{1}{V_{BZ}} \int_{BZ} A(k)dk \approx \sum_{k} \omega_k A(k) \tag{18}$$

where the integral is approximated by a sum over a number of k-points with weight ω_k. The Monkhorst-Pack grid [161] is a common technique used in sampling the Brillouin zone. This method generates special points in the Brillouin zone, and their integration weights provide an efficient means of integrating periodic functions in k-space. The accuracy of integration entirely depends on the choice of integration grid, and, therefore, the Monkhorst-Pack technique allows not only for specific integration of portions of Brillouin zone only, but also for a sampling of the entire Brillouin zone. However, the symmetry of the cell may drastically reduce the number of k- points within the Brillouin zone. If the supercell is large, the corresponding BZ is small, and few k-points are needed. In the non-periodic directions only the Γ-point ($k_i = 0$) is usually included.

Total Energy

Total energy is the key parameter for all DFT based calculations because it gives us useful information of many important properties of material. We can find many important properties as shown in Table 1 by taking derivatives of total energy with the parameters like lattice constant, volume of unit cell, atomic coordinates etc [162]. The plot between the total energy and finite lattice spacing gives the lattice constant which corresponds to the lowest energy. Total energy is also of importannce for finding the converged technical parameters such as, optimized value of number of k-points, cutoff energy for real space grid [163], optimal size of the basis set used etc., for any DFT code.

Table 1: The properties which can be calculated from total energy by taking derivatives with respect to different parameter [162].

Order of Derivatives	Parameters	Property
First	1. Atomic coordinates 2. Volume of unit cell 3. Electric field	1. Forces on respective atoms 2. Bulk Modulus 3. Dipole moment
Second	1. Lattice constant 2. Electric field	1. Infrared and Raman Spectra 2. Polarizibility
Third	1. Lattice constant 2. Lattice Constant and electric field	1. Anharmonic contributions to vibrational frequencies 2. Raman Intensity

Total and Partial Density of states

In the numerical calculations we repeatedly calculate total and partial densities of states. The density of states for a system described by the Hamiltonian matrix $\hat{H}$ is defined by

$$D(E) = \sum_i \langle \psi_i | \delta(E - \hat{H}) | \psi_i \rangle \tag{19}$$

where $|\psi_i\rangle$ is the eigenstates of the Hamiltonian $\hat{H}$. Above equation can be rewritten as:

$$D(E) = \sum_i \langle \psi_i | \psi_i \rangle \delta(E - \epsilon_i) \tag{20}$$

where ϵ_i are a discrete set of eigenenergies. This equation can be further written as

$$D(E) = \sum_i P_i D(E) \tag{21}$$

where $P_i D(E)$ is the partial density of states

$$P_i D(E) = \sum_j \langle \psi_j | i \rangle \langle i | \psi_j \rangle \delta(E - \epsilon_j) \tag{22}$$

Here the quantity $P_i D(E)$ expresses the density of states projected on to $|i\rangle$.

Dielectric Properties

SIESTA uses first order perturbation theory to calculate the dielectric properties of materials/molecules [145, 151]. One solves a problem of a photon perturbing a model via a single particle Hamiltonian i.e. one starts with a model ground state Hamiltonian H_0 and add a perturbing potential V as $H = H_0 + V(r)$, where $H_0 = p^2/2m + U(r)$ and $V = V_{ext} + V_s$. In the formula, p is momentum operator, U is crystal potential, V_{ext} is time dependent perturbation and V_s is the screening interaction due to the perturbation. Thereafter, one solves the Liouville equation for the above system by splitting density matrix into ground state and perturbed part, which results into the following formula for dielectric function:

$$D = \int dk [\frac{n_f - n_i}{\epsilon_f - \epsilon_i} - \omega] \langle \psi_i^*(k) | p | \psi_f(k) \rangle \langle \psi_f^*(k) | p | \psi_i(k) \rangle \tag{23}$$

where n_i and n_f are initial and final occupation numbers respectively; ϵ_i, ϵ_f and ω are initial eigenvalues, final eigenvalues and impinging photon frequency respectively. The dielectric function(D) above is the solution within first order time dependent perturbation theory. The first order part comes from approximating the commutator of H with the perturbed density matrix in the Liouville equation. However, up to this point there is no exchange and correlation in the solution. To correct the lack of exchange and correlation, in SIESTA code, the eigenvalues and eigen functions in above formula are replaced with the ground state DFT eigenvalues and eigenfunctions. So that at least the energies and the s, p, d, f character of the eigenfunctions are much better and one is indeed able to get a very reasonable answer in many situations.

Motivation and Research Objectives

As discussed earlier that low dimensional systems are the systems of much interests due to their entirely different behavior than corresponding bulk counterparts. Nanoscience and consequent nanotechnologies have been dominated by low dimensional honeycomb structured carbon based materials in the last two decades. Graphene, a two dimensional (2D) honeycomb structure of carbon, has been studied in great detail by researchers [69–71, 166], but it has no band gap. However, many important applications in optics and transistor technology require a band gap, leading to vigorous research efforts to functionalize it to achieve band gap manipulation. However, in contrast, layered transition metal dichalcogenides (LTMDCs), e.g. MoS_2 monolayer, are emerging as competing materials for nanoelectronics due to interesting properties like the presence of a band gap, thermal stability up to 1,100 ^0C and the absence of dangling bonds. This recently culminated in the successful implementation of a monolayer MoS_2-based field effect transistor, with HfO_2 as a gate insulator [40].

Atomically thin MoS_2 has also been studied by optical spectroscopy and has been found as a new direct band gap semiconductor with gap of 1.8 eV [53]. This has raised tremendous interest in exploring the extraordinary properties of other monolayers of LTMDs. Moreover, these materials have honeycomb structures like graphene and same mechanical exfoliation technique [102] can be applied to these materials as was applied to extract single layer of C atoms i.e graphene. Also it has been shown recently by Coleman et. al. [39] that layered materials, such as MoS_2, $MoSe_2$, $MoTe_2$, WS_2, $TaSe_2$, $NbSe_2$, $NiTe_2$, BN, Bi_2Te_2 can be efficiently exfoliated into individual layers. On the other hand, Pt deposited on a Ge(001) surface spontaneously forms nanowire arrays [109–111]. These nanowires are thermodynamically stable and can be hundreds of atoms long. The nanowires only occur on a reconstructed Pt-Ge surface where they fill the troughs between the dimer rows on the surface [74, 75]. This unique connection between the nanowires and underlying substrate make a thorough understanding of the reconstruction desirable for nanowires array and physical phenomenon associated with them.

The goal of this work is to obtain insight, from first principle calculations, on the properties and phenomena of layered transition metal dichalcogenides and semiconductor Germanium surfaces. Particularly, we would concentrate our efforts on systems with relevance and importance for experimental groups as well as for technological point of view. The objectives of our research work are as follows:

1. The first principle DFT based calculations will be caried out to find the electronic structure of the monolayers of LTMDCs MX_2 where M=Mo, W, Nb and X=S, Se, Te. However, our aim will not be calculate the correct band gap as it is well understood that conventional DFT approach is unable to yield correct band gap but our emphasis will be on the study of electronic structure of these monolayers with focus on the prediction of the nature of band gap of these monolayers.

2. As the quantum confinement can play important role on these materials, the next task will be to study the electronic structure of these materials by systematic reducing the number of layers from bulk to monolayer limit.

3. The optical properties of the monolayers of the considered materials would be interesting to look into in comparison with their bulk counterparts. However, it is worth mentioning that though many body effects may be important for correctly describing the excitonic effects, but the general insight about the dielectric functions and plasmons may be important.

4. Further the influence of quantum confinement effect on the dielectric properties by systematically reducing the number of layers from bulk to the monolayer limit will be looked into.

5. Next task will be the tuning of the electronic band gap and dielectric properties of the considered monolayers by using mechanical strains. Furthermore, electronic structure tuning of bilayers of these materials can be performed by number of ways like applying mechanical strain, tuning the interlayer distances, by applying external electric field etc.

6. After that, our aim is to investigate electron transport properties of these materials which can have technological importance, an area in which not much work has been done.

7. Besides, our aim is also to find atomic structure models for the adsorption of Pt on Ge(001) surface. Different types of Pt induced reconstructed geometry with varying the coverage of Pt will be studied for structural, electronic and dielectric properties. Also, efforts will be made to find electronic and dielectric properties of Pt/Ge interface by passivating with H atoms.

Bibliography

[1] S. Kim, A. Konar, W. Hwang, J. H. Lee, J. Lee, J. Yang, C. Jung, H. Kim, J. Yoo, J. Choi, Y. W. Jin, S. Y. Lee, D. Jena, W. Choi and K. Kim, *Nature Comm.* **3**, 1011 (2012).

[2] Q. H. Wang, K. Kalantar-Zadhe, A. Kis, J. N. Colemn and M. S. Strano, *Nature Nanotech.* **7**, 699 (2012).

[3] A. Castellanos-Gomez, M. Poot, G. A. Steele, H. S. J. van der Zant, N. Agrait and G. Rubio-Bollinger, *Adv. Mater.* **24**, 772 (2012).

[4] H. Fang, S. Chuang, T. C. Chang, K. Takei, T. Takahashi and A. Javey, *Nano Lett.* **12**, 3788 (2012).

[5] Y. Zhang, J. Ye, Y. Matsuhashi and Y. Iwasa, *Nano Lett.* **12**, 1136 (2012).

[6] H. R. Gutierrez,N. Perea-Lopez, A. L. Elias, A. Berkdemir, B. Wang, R. Lv, F. Lopez-Urias, V. H. Crespi, H. Terrones, and M. Terrones, *Nano Lett.* dx.doi.org/10.1021/nl3026357 (2012).

[7] Y. Zhou, Z. Wang, P. Yang, X. Zu, L. Yang, X. Sun and F. Gao, *ACS Nano* **6**, 9727 (2012).

[8] G. Cunningham, M. Lotya, C. S. Cucinotta, S. Sanvito, S. D. Bergin, R. Menzel, M. S. P. Shaffer and J. N. Coleman, *ACS Nano* **6**, 3468 (2012).

[9] Z. Yin, H. Li, L. Jiang, Y. Shi, Y. Sun, G. Lu, Q. Zhang, X. Chen and H. Zhang, *ACS Nano* **6**, 74 (2012).

[10] K. Dolui, C. D. Pemmaraju and S. Sanvito, *ACS Nano* **6**, 4823 (2012).

[11] P. Johari and V. B. Shenoy, *ACS Nano* **6**, 5449 (2012).

[12] E. Scalise, M. Houssa, G. Pourtois, V. Afanasev and A. Stesmans, *Nano. Res.* **5**, 43 (2012).

[13] H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D. W. H. Fam, A. I. Y. Tok, Q. Zhang and H. Zhang, *small*, **8**, 63 (2012).

[14] P. Cudazzo, M. Gatti, and A. Rubio, *Phys. Rev. B*, **86**, 075121 (2012).

[15] T. Li, *Phys. Rev. B*, **85**, 235407 (2012).

[16] B. Chakraborty, A. Bera, D. V. S. Muthu, S. Bhowmic, U. V. Waghmare and A. K. Sood, *Phys. Rev. B*, **85**, 161403 (2012).

[17] S. Bhattacharyya and A. K. Singh, *Phys. Rev. B*, **86**, 075454 (2012).

[18] T. Cheiwchanchamnangij and W. R. L. Lambrecht, *Phys. Rev. B*, **85**, 205302 (2012).

[19] W. S. Yun, S. W. Han, S. C. Hong, I. G. Kim and J. D. Lee, *Phys. Rev. B*, **85**, 033305 (2012).

[20] C. Ataca and S. Ciraci, *Phys. Rev. B* **85**, 195410 (2012).

[21] E. Erdogan, I. H. Popov, A. N. Enyashin and G. Seifert, *Euro. Phys. J. B*, **85**, 33 (2012).

[22] H. Qiu, L. Pan, Z. Yao, J. Li, Y. Shi and X. Wang, *Appl. Phys. Lett.* **100**, 123104 (2012).

[23] B. Radisavljevic, M. B. Whitwick and A. Kis, *Appl. Phys. Lett* **101**, 043103 (2012).

[24] Q. Yue, S. Chang, J. Kang, X. Zhang, Z. Shao, S. Qin and J. Li, *J. Phys.: Condens. Matter*, **24**, 335501 (2012).

[25] M.Lin, L. Liu, Q. Lan, X. Tan, K. S. Dhindsa, P. Zeng, V. M. Naik, M. M. Cheng and Z. Zhou, *J. Phys. D: Appl. Phys.*, **45**, 345102 (2012).

[26] Q. Liu, L. Li, Y. Li, Z. Jao, Z. Chen and J. Lu, *J. Phys. Chem C* **116**, 21556 (2012).

[27] H. Pan and Y. Zhang, *J. Phys. Chem C* **116**, 11752 (2012).

[28] C. Ataca, H. Sahin and S. Ciraci, *J. Phys. Chem C* **116**, 8983 (2012).

[29] P. Lu, X. Wu, W. Guo and X. C. Zeng, *Phys. Chem. Chem. Phys.* **14**, 13035 (2012).

[30] Q. Yue, J. Kang, Z. Shao, X. Zhang, S. Chang, G. Wang and S. Qin, *Phys. Lett. A* **376**, 1166 (2012).

[31] E. S. Kadantsev and P. Hawrylak, *Solid Stat. Comm.* **152**, 909 (2012).

[32] H. Pan and Y. Zhang, *J. Mater. Chem* **22**, 7280 (2012).

[33] A. Castellanos-Gomez, M. Poot, G. A. Steele, H. S. J. van der Zant, N. Agrait and G. Rubio-Bollinger, *Nanoscale Res. Lett.* **7**, 233 (2012).

[34] H. Liu, J. Gu and P. D. Ye, *IEEE Elec. Devic. Lett* **33**, 1273 (2012).

[35] L. Liu, S. B. Kumar and Y. Ouyang and J. Guo, *IEEE Trans. Elec. Devic. Lett* **58**, 3042 (2012).

[36] F. Guller, C. Helman and A. M. Llois, *Physica B* **407**, 3188 (2012).

[37] F. Parhizgar, H. Rostami and R. Asgari1, *arXiv:1212.1318v1* (2012).

[38] H.Shi, H. Pan, Y. Zhang and B. I. Yakobson, *arXiv:1211.5653v1* (2012).

[39] J.N. Coleman, M. Lotya, A. O'Neill et. al., *Science* **331**, 568 (2011).

[40] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti and A. Kis, *Nature Nanotechnology* **6**, 147 (2011).

[41] P. Johari and V. B. Shenoy, *ACS Nano* **5**, 5903 (2011).

[42] A. Ramasubramaniam, D. Naveh and E. Towe, *Phys. Rev. B*, **84**, 205325 (2011).

[43] A. Molina-Sanchez and L. Wirtz, *Phys. Rev. B*, **84**, 155413 (2011).

[44] S. W. Han, H. Kwon, S. K. Kim, S. Ryu, W. S. Yun, D. H. Kim, J. H. Hwang, J. S. Kang, J. Baik, h. J. Shin and S. C. Hong, *Phys. Rev. B*, **84**, 045409 (2011).

[45] C. Ataca, H. Sahin, E. Akturk and S. Ciraci, *J. Phy. Chem. C* **115**, 3934 (2011).

[46] C. Ataca and S. Ciraci, *J. Phys. Chem. C* **115**, 13303 (2011).

[47] C. Ataca, M. Topsakal, A. Akturk and S. Ciraci, *J. Phys. Chem. C* **115**, 16354 (2011).

[48] S. Yang, D. Li, T. Zhang, Z. Tao and J. Chen, *J. Phys. Chem. C*, **116**, 1307 (2011).

[49] Y. Ma, Y. Dai, W. Wei, C. Niu, L. Yu and B. Huang, *J. Phys. Chem. C*, **115**, 20237 (2011).

[50] Y. Ding, Y. Wang, J. Ni, L. Shi, S. Shi and W. Tang, *Physica B*, **406**, 2254 (2011).

[51] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C. Y. Chim, G. Galli and F. Wang, *Nano Lett* **10**, 1271 (2010).

[52] C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone and S. Ryu, *ACS Nano* **4**, 2695 (2010).

[53] K.F. Mak, C. Lee, J. Hone, J. Shan and T.F. Heinz, *Phy. Rev. Lett.* **105**, 136805 (2010).

[54] H.S.S. Ramkrishana Matte, A. Gomathi, A.K. Manna, D.J. Late, R. Dutta, S.K. Pati and C.N.R. Rao, *Angew. Chem. Int. Ed.* **49**, 4059 (2010).

[55] H. He, K. Wu, R. Sa, Q. Li and Y. Wei, *Appl. Phys. Lett* **96**, 082504 (2010).

[56] A. Castellanos-Gomez, N. Agrait and G. Rubio-Bollinger, *Appl. Phys. Lett* **96**, 213116 (2010).

[57] R. Shidpour and M. Manteghian, *Nanoscale* **2**, 1429 (2010).

[58] J. Li, *Appl. Phys. A* **99**, 229 (2010).

[59] A. R. B. Mendez, F. L. Urias Yamauchi, M. Terrones and H. Terrones, *Nanotechnology* **20**, 325703 (2009).

[60] S. Lebegue and O. Eriksson, *Phy. Rev. B* **79**, 115409 (2009).

[61] Q. C. Sun, X. S. Yu, L. I. Vergara, R. Rosentsveig and J. L. Musfeldt, *Phy. Rev. B* **79**, 205405 (2009).

[62] R. Shidpour and M. Manteghian, *Chem. Phys.* **360**, 97 (2009).

[63] V. V. Ivanovskaya, A. Zobelli, A. Gloter, N. Brun, V. Serin and C. Colliex, *Phy. Rev. B* **78**, 134104 (2008).

[64] Y. Li, Z. Zhou, S. Zhang and Z. Chen *J. Am. Chem. Soc.* **130**, 16739 (2008).

[65] A. Enyashin, S. Gemming and G. Seifert, *Eur. Physical J.(special topic)* **149**, 103 (2007).

[66] T. Li and G. Galli, *J. Phys. Chem C* **111**, 16192 (2007).

[67] A. Ayari, E. Cobas, O. Ogundadegbe and M. S. Fuhrer, *J. Appl. Phys* **101**, 014507 (2007).

[68] T. Ando, A. B. Fowler and F. Stern, *Rev. Mod. Phys.* **54**, 437 (1982).

[69] A.K. Geim and K.S. Novoselov, *Nat. Mater.* **6**, 183 (2007).

[70] A.K. Geim, *Science* **324**, 1530 (2009).

[71] C.N.R Rao, A.K. Sood, K.S. Subrahmanyam and A. Govindraj, *Angew. Chem. Int. Ed.* **48**, 7752 (2009).

[72] M. Leiber *MRS Bull.* **28** , 486 (2003) .

[73] J.C. Charlier, X. Blase and S. Roche. *Rev. Mod. Phys.* **79**, 677 (2007).

[74] A. A. Stekolnikov, F. Bechstedt, M. Wisniewski, J. Schafer and R. Claessen, *Phys. Rev. Lett* **100**, 196101 (2008).

[75] A. A. Stekolnikov, J. Furthmuller and F. Bechstedt, *Phys. Rev. B* **78**, 155434 (2008).

[76] Danny E.P. Vanpoucke, Geert Brocks, *arXiv:0901.2973v1* (2009), *ibid arXiv:0901.2969v1* (2009).

[77] Danny E.P. Vanpoucke, Geert Brocks, *Phy. Rev. B* **81**, 085410 (2010) *ibid* **81**, 035333 (2010).

[78] C. Kittle, *Introduction to Solid State Physics*, 7^{th} edition, Wiley, New York (1996).

[79] W. A. Harrison, *Electronic Structure and the Properties of Solids*, Freeman, (1980).

[80] J. M. Zimen, *Principles of the Theorie of Solids*, 2^{nd} edition, Cambridge, (1972).

[81] R. M. Martin, *Electronic Structure: Basic Theory and Practical Methods*, Cambridge University Press (2004).

[82] D. S. Sholl and J. N. Steckel, *Density Functional Theory: A Practical Introduction*, Wiley, New York (2009).

[83] J. Wilson and A. D. Yoffe, *Adv. in Phys.* **18**, 193 (1969).

[84] L.F. Matthesis, *Phy. Rev. Lett.* **30**, 784 (1973).

[85] L. F. Mattheiss, *Phy. Rev. B* **8**, 3719 (1973).

[86] A. D. Yoffe, *http://pubs.rsc.org — doi:10.1039/CS9760500051* (1976).

[87] K. Kam and B. Parkinson, *J. Phy. Chem.* **86**, 463 (1982).

[88] R. Tenne and A. Wold, *App. Phy. Lett.* **47**, 707 (1985).

[89] R. Coehoorn, C. Hass and R.A. Degroot, *Phy. Rev. B* **35**, 6203 (1987).

[90] W. G. Dawson and D. W. Bullett, *J. Phys. C.: Solid Stat. Phys.* **20**, 6159 (1987).

[91] K. Kobayashi and J. Yamauchi, *Phy. Rev. B* **51**, 17085 (1995).

[92] W. Sienicki and T. Hryniewicz, *Solar Energy Materials And Solar Cells* **43**, 67 (1996).

[93] P. Raybaud, G. Kresse, J. Hafner and H. Toulhoat, *J. Phys.:Condens. Matter* **9**, 11085 (1997).

[94] J. Wilcoxon, T. Thurston and J. Martin, *J. Nanostructured Materials* **12**, 993 (1999).

[95] G. Seifert, H. Terrones, M. Terrones, G. Jungnickel and T. Frauenheim *Phy. Rev. Lett* **85**, 146 (2000).

[96] T. Boker, R. Severin, A. Muller, C. Janowitz, R. Manzke, D. Vob, P. Kruger, A. Mazur and J. Pollmann, *Phy. Rev. B* **64**, 235305 (2001).

[97] A.H. Reshak and S. Auluck, *Phy. Rev. B* **68**, 125101 (2003).

[98] A. H. Reshak and S. Auluck, *Phy. Rev. B* **68**, 195107 (2003).

[99] A.H. Reshak and S. Auluck, *Phy. Rev. B* **71**, 155114 (2005).

[100] R. R. Chianelli. m. H. siadati and M. P. De la Rosa, *Catal. Revs.* **48**, 1 (2006).

[101] N. D. Boscher, Claire, J. Carmalt and I. P. Parkin, *J. Mater. Chem.* **16**, 122 (2006).

[102] K. Novoselov, D. Jiang, F. Schedin, T. Booth, V. Khotkevich, S. Morozov and A. Geim, *Proc. Natl. Acad. Sci., USA* **102**, 10451, (2005).

[103] A.R Beal, J.C. Knights and W.Y. Liang, *J. Phys. C.: Sol. Stat. Phys.* **5**, 3540 (1972).

[104] A.R Beal and H.P. Hughes, *J. Phys. C.: Sol. Stat. Phys.* **12**, 881 (1979).

[105] H.P Hughes and W.Y. Liang, *J. Phys. C.: Sol. Stat. Phys.* **7**, 1023 (1974).

[106] E. Fortina and F. Raga, *Phy. Rev. B* **11**, 905 (1975).

[107] K. Zeppenfeld, *Optics Communications* **1** 377 (1970).

[108] W.Y. Liang and S. L. Cundi , *Phis. Mag.* **19**, 1031 (1969).

[109] O. Gurlu, O. A. O. Adam, H.J.W. Zandvliet and B. Poelsema, *App. Phys. Lett.* **83** 4610 (2003).

[110] O. Gurlu, H. J. W. Zandvliet and Bene Poelsema, *Phy. Rev. B* **70**, 085312 (2004).

[111] O. Gurlu, H. J. W. Zandvliet and Bene Poelsema, *Phy. Rev. Lett.* **93**, 066101 (2004).

[112] N. Oncel, W. J. van Beek, B. Poelsema and H. J. W. Zandvliet *New J. Phys.* **9**, 449 (2007).

[113] U. Schwingenschlogl and C. Schuster, *Euro. Phys. J. B* **60**, 409 (2007).

[114] G. P. Srivastava, *Rep. Prog. Phys.* **60**, 561 (1997).

[115] H.J.W Zandvliet, *Rev. Modren Phys.* **72**, 593 (2000).

[116] H. J. W. Zandvliet, *Phys. Rep.* **388**, 1 (2003).

[117] K. Nakatsuji, Y. Takagi, F. Komori, H. Kusuhara and A. Ishii, *Phys. Rev. B* **72**, 241308 (1998).

[118] M. Nishida, *J. Phys. C.: Solid Stat. Phys.* **11**, 1217 (1978).

[119] F Jona, H.D. Shih. D. W. Jepsen and P. M. Marcus, *J.Phys. C.:Solid State. Phys.* **12**, L455 (1979).

[120] J. C. Fernandez, W.S. Yang, H. D. Shih, F. Jona, D. W. Jepsen and P. M. Marcus, *J. Phys. C: Solid Stat. Phys.* **14**, L55 (1981).

[121] S.D. Kevan and N.G. Stoffel, *Phy. Rev. Lett.* **53**, 702 (1984).

[122] S.D. Kevan, *Phy. Rev. B* **32**, 2344 (1985).

[123] J. Pollmann P. Kruger and A. Mazur, *J. Vac. Sci. Technol. B* **5**, 945 (1987).

[124] N. Roberts and R.J. Needs, *Surface Science* **236**, 112 (1990).

[125] L. Kipp, R. Manzke and M. Skibowski, *Solid State Commun.* **93** 603 (1995).

[126] Sato, M. Iwatsuki and H. Tochihara, *J. Electron Micros.* **48**, 1 (1999).

[127] M. Cakmak, G. P. Srivastava and S. Ellialtioglu, *Phys. Rev. B* **67**, 205314 (2003).

[128] W.Zhu, H. H. Weitering, E. G. Wang, E. Kaxiras and Z. Zhang, *Phys. Rev. Lett.* **93**, 126102 (2004).

[129] X. H. Zhou, X. S. Chen, L. Z. Sun and W. Lu, *J. Phy. D: Appl. Phys.* **38**, 1055 (2005).

[130] P. W. Loscutoff and S. F. Bent, *Annu. Rev. Phys. Chem* **57**, 467 (2006).

[131] A. van Houselt, R. van Gastel, B. Poelsema and H. J.W. Zandvliet, *Phy. Rev. Lett.* **97** ,266104 (2006).

[132] M.W. Radny, G.A. Shah, P.V. Smith, S.R. Schofield and N.J. Curson, *Phy. Rev. Lett.* **100**, 246807 (2008).

[133] X. F. Lin, K. J. Wan, J. C. Glueckstein and J. Nogami, *Phys. Rev. B* **47**, 3671 (1993).

[134] T. Shimakura, H. Minoda, Y. Tanishiro and K. Yagi, *Surf. Sci.* **407**, L657 (1998).

[135] M. Kageshima, Y. Torii, Y. Tano, O. Takeuchi and A. Kawazu, *Surf. Sci.* **472**, 51 (2001).

[136] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1113 (1965).

[137] W. Kohn, Noble Lectures:*Electronic Structure of Matter-Wave Functions and Density Functionals*, *Rev. Mod. Phys.* **71**, 1253 (1999).

[138] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos,*Rev. Mod. Phys* **64**, 1045 (1992).

[139] Lecture Notes of Prof. M. K. Harbola delivered in: *Seminar cum Workshop on First Principle and Other Simulation Methods in Condensed Matter Physics*, March 22-29, 2010, Himachal Pradesh University, Shimla, H.P., India.

[140] J. P. Perdew, A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).

[141] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

[142] P. E. Blochl, *Phys. Rev. B* **50**, 17953 (1994).

[143] P. Blaha et. al., WIEN2k,*An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties*, Technical University of Vienna (2001).

[144] http://elk.sourceforge.net/

[145] http://www.uam.es/siesta

[146] http://www.castep.org

[147] P. Ordejon, D. A. Darbold, R. M. Martin and M. P. Grumbach, *Phys. Rev. B* **51** , 1456 (1994).

[148] P. Ordejon, E. Artacho and J.M. Soler, *Phys. Rev. B* **53** , 10441 (1996).

[149] D. Sanchez-Portal, P. Ordejon, E. Artacho and J.M. Soler, *Int. J. Quantum Chem.* **65**, 453 (1997).

[150] E. Artacho, D. Sanchez-Portal, P. Ordejon, A. Garcia and J.M. Soler, *Phys. Stat. Sol. (b)* **215**, 809 (1999).

[151] J.M. Soler, E. Artacho, J. D. Gale, A. Garc1ia, J. Junquera, P. Ordejon and D. Sanchez-Portal, *J.Phys.:Condens. Matter* **14**, 2745 (2002).

[152] D. Sanchez-Portal, E. Artacho and J.M. Soler,*J. Phys.: Condens. Matter* **8**, 3859 (1996).

[153] J. Junquera, O. Paz, D. Sanchez-Portal and E. Artacho,*Phys. Rev. B* **64**, 235111 (2001).

[154] T. Ozaki,*Phys. Rev. B* **67**, 155108 (2003).

[155] T. Ozaki and H. Kino,*Phys. Rev. B* **69**, 195113 (2004).

[156] W. E. Pickett, *Pseudopotential Methods in Condensed Matter Applications*, An international review journal devoted to methods and algorithms in computational physics, **9**, 115-198 (1989).

[157] D.R. Hamann, M.Schluter and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).

[158] G.P. Kerker, *J.Phys.C.:Solid St. Phys.* **13** , L189 (1980).

[159] N. Troullier and J. L. Martins, *Phy. Rev. B* **43**, 1993 (1991).

[160] N. Troullier and J. L. Martins, *Phy. Rev. B* **43**, 8861 (1991).

[161] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).

[162] www.home.uni-osnabrueck.de/apostnik/

[163] J. Moreno and J.M. Soler, *Phys. Rev. B* **45**, 13891 (1992).

[164] M. Brandbyge, J. L. Mozos, P. Ordejon, J. Taylor and K. Stokbro, *Phys. Rev. B* **65**, 165401 (2002).

[165] SIESTA User manual.

[166] O.V. Sedelnikova, L.G. Bulusheva and A.V. Okotrub, J. Chem. Phys. **134**, 244707 (2011).

List of Publications

Paper Published/Communicated in International Journals

1. **Ashok Kumar** and P.K. Ahluwalia *"Semiconductor to Metal Transition in Bilayer Transition Metal Dichalcogenides MX_2 (M=Mo,W; X=S,Se,Te)"* (Submitted).

2. **Ashok Kumar** and P.K. Ahluwalia *"Mechanical Strain Dependent Dielectric Properties of Two-Dimensional Honeycomb Structure of MoX_2 (X=S,Se,Te)"* Physica B (To be Submitted in Revised Form).

3. **Ashok Kumar** and P.K. Ahluwalia *"Effect of Quantum Confinement on Electronic and Dielectric Properties of NbX_2 (X= S, Se,Te)"* Journal of Alloys and Compounds 550 (2013) 283-291.

4. **Ashok Kumar** and P.K. Ahluwalia *"Electronic Structure of Transition Metal Dichalcogenides Monolayers 1H-MX_2 (M=Mo,W; X=S,Se,Te) from Ab-initio Theory: New Direct Band Gap Semiconductors,* European Physical Journal B 85 (2012) 186.

5. **Ashok Kumar** and P.K. Ahluwalia *"A First Principle Comparative Study of Electronic and Optical Properties of 1H-MoS_2 and 2H-MoS_2"* Materials Chemistry and Physics 135 (2012) 755-761.

6. **Ashok Kumar** and P.K. Ahluwalia *"Tunable Dielectric Response of Transition Metal Dichalcogenides MX_2 (M = Mo, W; X= S, Se,Te)"* Physica B: Condensed Matter 407 (2012) 4627-4634.

7. **Ashok Kumar** and P.K. Ahluwalia *"Ab-initio Study of Platinum Induced Reconstructions on Ge(001)-(1×2) Surface"* Physica B:Condensed Matter 406 (2011) 4691-4699.

Paper Presented in International/National Conferences/Symposiums and Published in International/National Proceedings

1. **Ashok Kumar**, Brij Mohan, Arun Kumar and P.K.Ahluwalia *"Mechanically Strained Tuning of the Electronic and Dielectric Properties of Monolayer Honeycomb Structure of Tungsten Disulphide(WS_2)"* AIP Conference Proceedings(accepted for publication), also presented in "57th DAE Solid State Physics Symposium (DAESSPS-2012)" Dec. 03-07 (2012), Indian Institute of Technology, Bombay, India.

2. **Ashok Kumar** and P.K. Ahluwalia *"Exotic Properties of Layered Molybdenum Disulfide (MoS_2): A Promising Nanomaterial"* presented in "National Seminar on Experimental and Computational Techniques in Material Science (ECTMS-2012)" March 31-April 2, 2012, Himachal Pradesh University, Shimla, H.P, India.

3. **Ashok Kumar**, Jagdish Kumar and P.K.Ahluwalia *"Electronic Structure and Optical Conductivity of 2D-MoS_2: Pseudopotential DFT versus Full Potential Calculations"* AIP Conference Proceedings 1447 (2012) 1269-1270, also presented in "56th DAE Solid State Physics Symposium (DAESSPS-2011)" Dec. 19-23 (2011), SRM University, Kattanakulthur, Tamilnadu, India.

4. **Ashok Kumar**,Jagdish Kumar and P.K.Ahluwalia *"Dimer Induced Reconstruction and Metallicity of Ge(001) surface: Ab-initio SIESTA Study"* AIP Conference Proceedings 1349 (2011) 629-630, also presented in "55th DAE Solid State Physics Symposium (DAESSPS-2011)" December 26-30, 2010, Manipal University, Manipal, Karnatka, India.

5. **Ashok Kumar**, Brij Mohan and P.K.Ahluwalia *"Ab-initio Study of Homo and Hetro Platinum Dimers on Ge(001)-(2x1) Surface"* AIP Conference Proceedings 1393 (2011) 195-196, also presented in "International Conference on Advances in Condensed and Nano Materials (ICACNM-2011)" February 23-26, 2011, Punjab University Chandigarh, Chandigarh, India.

International/National School/Workshops Attended

1. *"International Summer School on New Trends in Computational Approaches for Many Body Systems"* May 28-June 08, 2012, University de Sherbrooke, Sherbrooke, Quebec, Canada.

2. *"National Workshop on Advanced Characterization and Simulation Techniques (ACST-2012)"* March 12-17, 2012, Kurukshetra University, Kurukshetra, Haryana, India.

3. "Workshop on Parallel Computing using HPCC" March 2-3, 2012, Punjab University Chandigarh, Chandigarh, India.

4. *"Seminar cum Workshop on First Principle and Other Simulation Methods in Condensed Matter Physics"* March 22-29, 2010, Himachal Pradesh University, Shimla, H.P., India.

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